

NASA Contractor Report 181807

**CHEMOVISCOSITY MODELING FOR THERMOSETTING
RESIN SYSTEMS - IV**

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**(NASA-CR-181807) CHEMOVISCOSITY MODELING
FOR THERMOSETTING RESIN SYSTEMS, 4
(Planning Research Corp.) 51 p CSCL 11D**

N89-21839

**Unclas
G3/24 0200241**

Contract NAS1-18000

March 1989



**National Aeronautics and
Space Administration**

**Langley Research Center
Hampton, Virginia 23665-5225**

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FOREWORD

This work was performed at the Polymeric Materials Branch (PMB), NASA Langley Research Center (LaRC). This is a progress report on an ongoing research project toward the understanding of reaction advancements and resin flow properties during processings of thermosetting materials in an autoclave environment. R. M. Baucom (PMB) was the technical monitor. Three earlier reports concerning the same subject matter were:

1. Chemoviscosity Modeling For Thermosetting Resin Systems - I, NASA Contractor Report CR-172443, November, 1984.
2. Chemoviscosity Modeling For Thermosetting Resin Systems - II, NASA Contractor Report CR-177958, August, 1985
3. Chemoviscosity Modeling For Thermosetting Resin Systems - III, NASA Contractor Report CR-181718, August, 1988

The authors would like to acknowledge financial support of NASA through Contract NAS1-18000 to Emhart PRC, and Research Grant NAG-1-569 to the Department of Mechanical Engineering and Mechanics, Old Dominion University, Norfolk, Virginia. W. T. Freeman (AMB) who provided the materials and Dr. J. A. Hinkley (PMB) who reviewed the entire manuscript prior to its publication are also gratefully acknowledged.

CHEMOVISCOSITY MODELING FOR THERMOSETTING RESIN SYSTEMS - IV

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ABSTRACT

An experimental study on the changes of chemorheological properties has been conducted and analyzed on a commercial Hercules 3501-6 resin system cured under several isothermal conditions between 375 and 435 °K. For cure temperatures ≥ 385 °K, the storage modulus curing curves, $G'(t)$, exhibited abrupt changes in slope which occurred at various times depending on the curing temperatures. These slope changes were attributed to the onset of gelation reactions. Crossover points between $G'(t)$ and $G''(t)$ curves were observed for curing temperatures ≥ 400 °K. The gelation and the crossover points obtained from the chemorheological measurements, therefore, defined two characteristic resin states during cure. Approximately the same value of the degree of cure was reached by the advancement of reaction in each of these states. The temperature dependency of the viscosities in the characteristic resin states, and the rate constants of increase in moduli at different stages of curing were analyzed. Various $G'(t)$ and $G''(t)$ isothermal curing curves were also shown to be capable of being superimposed to one another by the principle of time-temperature superposition. The resultant shift factors $a_t(T)$ and $a_\eta(T)$ were shown to follow Arrhenius type relationships. Values of the activation energy suggested that the reaction kinetics, instead of the diffusion mechanism, was the limiting step in the overall resin advancement for cure at temperatures ≥ 385 °K.

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LIST OF SYMBOLS

| | |
|----------------|--|
| $a_t(T)$ | $=t(T)/t(T_r)$, shift factor in reaction time, defined by Eq. (6) |
| $a_\eta(T)$ | shift factor in viscoelastic properties defined by Eq. (7) |
| E_a | Apparent activation energy (kcal/mole) of polymerization reaction |
| E_η | Activation energy (kcal/mole) for viscous flow |
| G'' | Loss modules (dyne/cm ²) |
| G' | Storage modulus (dyne/cm ²) |
| G^* | Complex modulus $(G'^2 + G''^2)^{1/2}$ (dyne/cm ²) |
| k | Reaction rate constant (min ⁻¹) |
| T_r | Reference temperature (°K) |
| t | Reaction time (minute) |
| η^* | Complex viscosity (poise) |
| ω | Frequency (rad/sec) |
| $\alpha(t)$ | Degrees of cure defined by the fraction of heat released at time t |
| $\dot{\gamma}$ | Steady state shear rate (sec ⁻¹) |

Subscripts

| | |
|------|---|
| o | Gelation point or the onset of abrupt change in slope of $G'(t)$ curing curve |
| c | Crossover point between $G'(t)$ and $G''(t)$ curves |
| po | Post gelation point |
| pc | Post crossover point |

INTRODUCTION

Rheology is a science that deals with the deformation and flow of material under stress. Understanding the rheological properties of polymeric materials has played an increasingly critical role for the successful processing of such materials. For thermoplastic melt, the viscoelastic properties are determined by processing temperatures and flow geometry. In the processing of thermosetting resin, chemorheology is influenced by one additional factor, i.e., reaction kinetics of the resin system. Processing temperature affects the chemoviscosity rise profile in two opposing ways. Increases in temperature will not only cause the chemoviscosity to decrease at a given extent of reaction, but will also increase the reaction rate, which results in an increase in the resin viscosity. It is therefore essential to obtain chemorheology data as a function of reaction kinetics and temperature for the purposes of material characterization and process modeling. Unlike more conventional characterization techniques, such as stoichiometry, calorimetry and spectrometry, the measurements of properties of chemorheology are directly useful to the processing engineer who is concerned with the behavior of resin flow [1 - 3]. It is well known that viscoelastic properties are sensitive to the changes in macromolecular chain length. During the cure of thermosetting resins, the structure of the resin polymer undergoes continuous phase transformations from a low molecular weight liquid to a high molecular weight melt and eventually transforms to a crosslinked network. Changes in the slopes of viscoelastic properties versus reaction time curves should directly reflect such phase transformations within the material. By neglecting the effects of temperature dependence, it is even possible to relate the viscoelastic property-time profiles to the reaction kinetics of the resin system under cure.

In this paper we report an experimental study of the changes in rheological properties of a thermosetting resin system cured under several isothermal conditions.

MATERIAL

As received commercial Hercules 3501-6* epoxy resin was used without further treatments in this study. This material was selected because of its wide useage in the aerospace industry. The Hercules 3501-6 epoxy contains concentrations of following starting components [5]:

| Component | wt % |
|----------------------------------|------|
| Tetraglycidal Methylenedianiline | 56.5 |
| Alicyclic Diepoxy Carboxylate | 9.0 |
| Epoxy Cresol Novolac | 8.5 |
| 4,4' Diaminodiphenyl Sulfone | 25.0 |
| Boron Trifluoride Amine Complex | 1.1 |

Test samples were preconditioned at room temperature by pressing between two pieces of non-porous Teflon cloth to produce flat sheets with given uniform thickness. A resin wafer of 1.2 mm in thickness and 1.25 cm in diameter was then made with a steel guide. All samples were stored at -5 °C before being loaded in the Rheometer for rheological measurements.

*Hercules 3501-6 resin is manufactured by the Hercules Corp.

EXPERIMENT

A Rheometrics System 4 rheometer incorporated with a parallel-plate test fixture was used for the rheological measurements. The test sample was confined in the gap between two parallel plates with 1.25 cm in radius. The top plate was oscillated at a given frequency and amplitude, while the bottom plate was mounted on a torque transducer for force measurements. The typical gap between the plates was 1.2 mm. The plates and test samples were enclosed in a heat chamber purged with nitrogen gas. The test chamber was always preheated to the test temperature before loading the sample to insure precise gap settings.

The oscillating amplitude level was selected to assure that the strains imposed onto the sample during measurement were within its linear viscoelastic response range while maintaining adequate torque values. A typical measurement on this particular resin system usually started at 0.5 strain level. The strain value was stepwisely decreased down to about 0.001 in accordance with the increasing rigidity of the sample during the entire cure cycle. Plate oscillatory motion was set at a frequency of $\omega = 10$ rad/sec. Repeatability of the measurements performed at each cure temperature was always checked by selecting various strain values during the cure cycle. The recorded cyclic torque values were decomposed into in-phase and out-of-phase components with respect to the oscillatory deformation imposed on the sample. The corresponding storage (G') and loss (G'') moduli were obtained from these information. The complex viscosity, η^* , was then calculated directly from $\eta^* = (G'^2 + G''^2)^{1/2}/\omega$.

RESULTS AND DISCUSSION

Rheological measurements were made isothermally on the Hercules 3501-6 resin system at six selected temperatures between 370 to 435 °K. Typical double logarithmic plots for the storage, $G'(t)$, and loss, $G''(t)$, moduli as functions of reaction time, t , at 375, 385, 400, 410, 425 and 435 °K are shown in Figures 1-6, respectively. Moduli measurements ranged from 10 to 10^7 dynes/cm². Measured values above 10^7 dynes/cm² are not reported in the Figures, due to the considerations of possible slippage between the rigid sample and the tool plates at the latter stages of curing in the Rheometer using parallel-plate geometry. The loss moduli were observed to increase smoothly over the entire cure cycle. In contrast, however, the storage moduli, $G'(t)$, exhibited abrupt changes in slope at different curing times for samples cured at temperatures above 375 °K. As the cure temperature increases, the abrupt change in slope occurs earlier in the cure cycle.

Another characteristics of the curing behavior of Hercules 3501-6 epoxy is that the $G'(t)$ and $G''(t)$ curves crossover at certain curing times at temperatures above 385 °K. The G' and G'' coincide over a period of time during cure at 400 °K. A single crossover point, however, was observed by contrast when higher curing temperatures were employed. Some properties associated with these curing characteristics are summarized in Tables 1 and 2. The subscript 'o' refers to the onset of the abrupt change in $G'(t)$, and the subscript 'c' denotes the crossover point between the $G'(t)$ and $G''(t)$ curves.

Lee et al [6] reported DSC thermal analysis data on the same resin system cured under isothermal conditions. The degree of cure $\alpha(t)$ was defined as fraction of heat released at time t . The following equations were found to describe the degree of cure α rather satisfactorily:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1 - \alpha)(B - \alpha) \quad \text{for } \alpha < 0.3 \quad (1a)$$

$$\frac{d\alpha}{dt} = K_3(1 - \alpha) \quad \text{for } \alpha > 0.3 \quad (1b)$$

where

$$K_1 = A_1 \text{Exp}(-\Delta E_1/RT),$$

$$K_2 = A_2 \text{Exp}(-\Delta E_2/RT),$$

$$K_3 = A_3 \text{Exp}(-\Delta E_3/RT).$$

Values of the constants are summarized in Table 3. Values of α_o and α_c calculated from Eqs. (1a, b) are also included in Tables 1 and 2 for samples cured at various specified isothermal conditions.

Gelation Point

The gel point of a crosslinking polymer is referred to as a gel state reached by the advancement of reactions during cure. At the molecular level, a gel is formed when at least one of the molecules has grown very large and its size reaches dimensions on the order of the macroscopic sample [7]. Determination of the gel point varies according to resin properties measured. In the steady state shear experiment, for example, the gel point is commonly defined as the time when shear viscosity becomes infinite, or when the equilibrium modulus becomes nontrivial [2-3]. In practice, however, the gel point is determined at the point when the steady shear viscosity reaches 10^3 poises and the resin ceases to flow readily. In the dynamic experiment, the gel point is located by the crossover point between the $G'(t)$ and $G''(t)$ curves [8]. Recently, Winter et al. has suggested a constitutive equation for network polymers at the gel point [9,10]. The constitutive equation shows that the crossover points where $G'(\omega) = G''(\omega)$ are indeed a rheological property at the gel point for the Polydimethylsiloxane (PDMS) polymer used in their experiments [9].

Experimentally measured $G'(t)$ and $G''(t)$ for the Hercules 3501-6 resin system cured at different isothermal conditions are shown in Figures 5 and 6. At temperatures below 385 °K (375

°K cure, for example), neither the abrupt change in slope of the $G'(t)$ curve nor the crossover point was observed (see Figure 1), and the resin will not gel at any point in the entire cure cycle. At 385 °K, a distinct change in slope of the $G'(t)$ curve was observed. Since storage modulus G' is a measure of resin elasticity, a dramatic increase in $G'(t)$ indicates the initiation of a gelation network. However, $G'(t)$ is consistently lower than $G''(t)$ over the entire cure cycle, with the largest G'/G'' equals to 0.625 which occurs at about $t = 400$ minutes (see Figure 2). For $T \geq 400$ °K, the curing curves possess not only a distinct change in slope of the $G'(t)$ but also a crossover point between $G'(t)$ and $G''(t)$. Consequently, it seems more appropriate to assign the gel point for the resin system studied here at the onset of the abrupt change in slope of the $G'(t)$ curing curves under these various isothermal curing conditions. It is noted that at the gel points, G' is much lower than G'' by almost two orders of magnitude, and the resin maintains basically in a viscoelastic liquid-like state.

It is conceivable that the occurrences of the gelation point and the crossover point for resin samples cured at various temperatures higher than 385 °K, define uniquely two common material states during the advancement of reactions. The nearly constant values of the observed α_o in Table 1 seems to support such rationalization. Values of α_c in Table 2 show larger scatters, and could be attributed to the extrapolation errors introduced by extending Eqs. (1) outside the range of α originally covered by the study of Lee et al. [6]. Variations of complex viscosities η_o^* and η_c^* in Tables 1 and 2 are therefore due to temperature effects.

Temperature Dependent Viscosities

In numerous studies of polymeric liquids, the complex viscosities $\eta^*(\omega)$ have been observed to closely resemble $\eta(\dot{\gamma})$, where $\eta(\dot{\gamma})$ is the steady shear viscosity at shear rate $\dot{\gamma}$. This relationship $\eta(\dot{\gamma}) = \eta^*(\omega)$ is known as Cox-Merz rule [11]. This rule has been proven to be very useful in predicting $\eta(\dot{\gamma})$ when only linear viscoelastic data are available [12]. Consequently the temperature dependent behaviors of viscosities η_o^* and η_c^* are investigated according to the following formula:

$$-(T - T_r) / \log a_T = (T - T_r) / C_1 + C_2 / C_1 \quad (2)$$

$$\eta^* = A \exp [E_\eta / R T] \quad (3)$$

Eq. (2) is derived from the Williams-Landel-Ferry (WLF) equation with $a_T = \eta^*(T)/\eta^*(T_r)$ [13]. C_1 and C_2 are material parameters, and $T_r = 400$ °K was selected as the reference temperature. Eq. (3) is the so-called Arrhenius type relationship. $R = 1.986$ cal/mole/°K is the ideal gas constant, and E_η is the activation energy for viscous flow. Eqs. (2) and (3) predict that the plot of $-(T - T_r) / \log a_T$ vs. $(T - T_r)$ or $\ln \eta^*$ vs. $(1/T)$ should be linear for temperature dependency following either the WLF type or the Arrhenius type, respectively.

Results of the linear Least Squares fit of Eqs. (2) and (3) to the experimental data (see Tables 1 and 2) are tabulated in Table 4. It is noted that $\eta^*(T)$ can be more accurately described by the Arrhenius type of temperature dependency in both characteristic resin states. This suggests that the glass transition temperature, T_g , of the material remains constantly less than approximately $(T_d - 100)$ °K up to the crossover point, t_c , of $G'(t)$ and $G''(t)$ during the advancement of resin system cured isothermally under each temperature T_d . Such behavior was indeed observed by the differential scanning calimetry thermal analysis conducted before on the same resin system [14].

Overall Reaction Kinetics Of Resin Advancement

It is also of interest to compare the activation energies of the polymerization reaction, E_a , and viscous flow, E_η , at the two characteristic material states during cure. Assuming that the inverse of reaction time, t , has the same temperature dependency as the overall reaction rate constant, k_p , then

$$t = 1 / k_p = A_t \exp [E_a / RT] \quad (4)$$

A semi-logarithmic plot of $\ln t$ vs. $(1/T)$ should yield the apparent activation energy of polymerization, E_a . Values of E_a , together with values of E_η obtained from Eq. (3) and Table 4 are summarized in Table 5. Within the range of curing temperatures investigated here, the higher value of E_a rather than E_η at the gelation point clearly suggests that the mechanism of chemical reaction is the limiting step for the rate of advancement of the resin system during cure. On the other hand, higher value of E_η than E_a at the crossover point suggests that the limiting step for the rate of resin advancement becomes diffusion controlled.

In the semi-logarithmic plots of $G'(t)$ and $G''(t)$ shown in Figures 7 and 8, the slopes of the curves represent the reaction rate constants, k , which dictate the rates of increase of the moduli. Also shown in the Figures are arrow marks which identify locations of the gelation and crossover points. For the curing temperatures $\geq 400^\circ\text{K}$, the crossover points become evident. It is noted that beyond the crossover points, both $G'(t)$ and $G''(t)$ curves are characterized by straight lines, which indicate the first order reaction. The slopes of these straight lines, k_{pc} , are tabulated in Table 6. It shows that values of $k_{pc,G'}$ are approximately equal to $k_{pc,G''}$, where the subscript 'pc' denotes 'post crossover', and the subscripts 'G' and 'G'' refer to the $G'(t)$ and $G''(t)$ curves, respectively.

Not far away into the cure beyond the gelation points, the semi-logarithmic plots of $G'(t)$ and $G''(t)$ are also characterized by straight lines as well. These straight lines span 2 to 3 orders of magnitude in moduli. The slopes, k_{po} , where subscript 'po' denotes 'post gelation', are also tabulated in Table 6. Ratios of $k_{po,G'}/k_{po,G''}$ are noted to vary between 2.00 to 2.33 under various isothermal curing temperatures.

For linear flexible polymers with sufficiently high molecular weight, M_w , such that the entanglement effects become evident, it is known in polymer rheology that $\eta_0 \propto M_w^{3.4}$ and $N_1 \propto M_w^{7.0}$ [12], where η_0 is the zero shear viscosity and N_1 is the first normal stress difference. N_1 and η_0 are similar to the storage $G'(\omega)$ and loss $G''(\omega)$ moduli, which measure elastic and dissipation factors respectively, for high polymers under deformation. From the relationships where $\eta_0 \propto G''(\omega)$ and $N_1(\dot{\gamma}) \propto G'(\omega)$, we have the ratio

$$\frac{k_{po,G'}}{k_{po,G''}} = \frac{d \log G'(t)/dt}{d \log G''(t)/dt} = 2.05 \quad (5)$$

The theoretical value of the ratio calculated by Eq. (5) compares very favorably to the experimentally observed values as previously discussed.

Correspondence Between Cure Temperature And Reaction Time

Double logarithmic plots of the curing curves for Hercules 3501-6 are shown in Figures 9 and 10. It was noted that the curing curves of either $G'(t)$ or $G''(t)$ under various isothermal conditions have similar shapes. Attempts had been made to shift the curing curves both horizontally and vertically with respect to the curve of a selected reference cure temperature. The selected reference temperature was $T_r = 400$ °K. A single master curve of $(\log G'')$ versus $(\log t)$ obtained by this method is shown in Figure 11. The capability for data to be superimposed is generally satisfactory, except that the data at the two highest temperatures (425 and 435 °K) are noted to consistently deviate from the main body of the master curve beyond the crossover points. The horizontal (reaction time) and vertical (modulus) shift factors $a_t(T)$ and $a_\eta(T)$, respectively are defined by

$$\log a_t(T) = \log t(T) - \log t(T_r), \quad (6)$$

and

$$\log a_\eta(T) = \log G''(T) - \log G''(T_r). \quad (7)$$

Values of $a_t(T)$ and $a_\eta(T)$ calculated from Eqs. (6) and (7) are tabulated in Table 7. The temperature dependency of the shift factors is plotted in Figure 8. Linear relationships are noted which suggest the adequacy of the following equations:

$$a_t(T) = A_t \text{Exp} [E_a/RT] \quad (8)$$

and

$$a_\eta(T) = A_\eta \text{Exp} [E_\eta/RT] \quad (9)$$

to describe the relationship, where R is the ideal gas constant and T is the cure temperature in $^{\circ}\text{K}$. E_a and E_η denote the overall apparent activation energy of polymerization reaction and the activation energy of viscous flow, respectively. An apparent change in slope of the $\log a_\eta(T)$ vs. $(1/T)$ plot occurs near $T = 385^{\circ}\text{K}$. By means of Least Squares fit to the data points in Figure 12, we have $E_a = E_\eta = 16.5$ kcal/mole for $T \leq 385^{\circ}\text{K}$, and $E_a = 16.5$ kcal/mole, $E_\eta = 5.60$ kcal/mole for $T > 385^{\circ}\text{K}$. The higher value of the apparent activation energy for the polymerization reaction for this particular resin system cured at temperatures above 385°K suggests that the chemical reaction mechanism is the overall limiting step for the advancement of the resin under isothermal curing conditions.

Applying the same shift factors $a_t(T)$ and $a_\eta(T)$ of the Table 6 to the storage modulus $G'(t)$, a single master curve can again be deduced as shown in Figure 13. This is expected since each of the viscoelastic properties, $G'(t)$ and $G''(t)$, were measured against the reactive resin advancement which originated from the same reaction mechanism. A less satisfactory result is noted, however, when comparing the master curve of $G'(t)$ with that of $G''(t)$ in Figure 11.

CONCLUSIONS

Measurements of the changes of rheological properties of the Hercules 3501-6 resin system cured under six isothermal conditions between 375 and 435 °K had been made on a Rheometrics System 4 rheometer. The changes in storage modulus $G'(t)$ and loss modulus $G''(t)$ curing curves were followed by small amplitude oscillatory dynamic experiments using a parallel-plate configuration.

Two characteristic material states were identified: the gelation point manifests itself by an abrupt change in slope of the $G'(t)$ curve at curing temperatures ≥ 385 °K; and the crossover point between $G'(t)$ and $G''(t)$ curves was observed at curing temperatures ≥ 400 °K. At each characteristic material state, the same degree of cure was reached for resin samples cured isothermally at different temperatures. The temperature dependence of viscosity in each of these two characteristic material states was shown to follow the Arrhenius type relationship, which suggested that the glass transition temperature, T_g , should remain constantly less than $(T_m - 100)$ °K up to the crossover point during the advancement of the resin under curing temperature T_m . Such behavior was also observed by DSC thermal analysis conducted on the same resin system. By comparing the activation energies of the polymerization reaction and the viscous flow at each characteristic material state, it was revealed that within the range of curing temperatures investigated here, the mechanism of chemical reaction was the limiting step for the rate of advancement of the resin system at the gelation point; while at the crossover point, the limiting step became diffusion controlled.

It was found that the curing behavior of the Hercules 3501-6 resin system under various temperatures can be unified by the technique of time-temperature superposition. The temperature dependent shift factors on both moduli and reaction time indicated that at $T \geq 385$ °K, the polymerization reaction kinetics was the limiting step for overall advancement of the reactive resin system. At curing temperatures below 385 °K, however, both the diffusion mechanism and the

reaction kinetics played equal roles. The method of rheological analysis discussed here should be useful in the processing of commercially interesting thermosetting materials.

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Table 1. Properties Associated with the Onset of Abrupt Change in Storage Moduli $G'(t)$ During the Isothermal Curing of Hercules 3501-6 Resin System

| T(°K) | t_0 (mins) | $G'_0(10^2 \text{ dyne/cm}^2)$ | $G''_0(10^3 \text{ dyne/cm}^2)$ | $\eta_0^*(10^2 \text{ poises})$ | α_0 |
|-------|--------------|--------------------------------|---------------------------------|---------------------------------|------------|
| 375 | - | - | - | - | - |
| 385 | 220 | 1.8 | 15.0 | 15.0 | 0.57 |
| 400 | 110 | 2.3 | 7.0 | 7.0 | 0.59 |
| 410 | 65 | 1.6 | 5.4 | 5.4 | 0.59 |
| 425 | 25 | 1.2 | 2.1 | 2.1 | 0.52 |
| 435 | 12 | 0.84 | 1.6 | 1.6 | 0.45 |

Table 2. Properties Associated with the Crossover Point Between $G'(t)$ and $G''(t)$ During the Isothermal Curing of Hercules 3501-6 Resin System

| T(°K) | t_c (mins) | $G'_c = G''_c(10^4 \text{ dyne/cm}^2)$ | $\eta_c^*(10^4 \text{ poises})$ | α_c |
|-------|--------------|--|---------------------------------|------------|
| 375 | - | - | - | - |
| 385 | - | - | - | - |
| 400 | 182 | 71.0 | 10.0 | 0.76 |
| 410 | 95 | 28.0 | 4.0 | 0.72 |
| 425 | 39 | 10.0 | 1.4 | 0.64 |
| 435 | 19 | 4.7 | 0.67 | 0.55 |

Table 3. Values of Constants in Eqs. (1a, b) for Hercules 3501-6 Resin System

$$B = 0.47$$

$$A_1 = 2.101 \times 10^9 \text{ min}^{-1}$$

$$A_2 = -2.014 \times 10^9 \text{ min}^{-1}$$

$$A_3 = 1.960 \times 10^5 \text{ min}^{-1}$$

$$\Delta E_1 = 8.07 \times 10^4 \text{ J/mole}$$

$$\Delta E_2 = 7.78 \times 10^4 \text{ J/mole}$$

$$\Delta E_3 = 5.66 \times 10^4 \text{ J/mole}$$

Table 4. Linear Least Squares Results of Eqs. (2) and (3) for the Temperature Dependence of Viscosities

| Resin State | Parameter* | WLF Type, Eq. (2) | Arrhenius Type, Eq. (3) |
|-----------------|------------|-------------------|-------------------------|
| Gelation Point | R_0 | 0.049 | 0.994 |
| | P_0 | 58.43 | 7.70 |
| | Q_0 | 0.045 | 12.71 |
| Crossover Point | R_c | 0.952 | 0.999 |
| | P_c | 23.51 | 13.19 |
| | Q_c | 0.195 | 21.54 |

*Subscripts '0' and 'c' refer to gelation point and crossover point respectively.

R_0, R_c denote correlation coefficients from Least Squares.

$P = C_2/C_1$ (degree) and $Q = 1/C_1$ in Eq. (2).

$P = E_\eta/R$ ($^{\circ}K$) and $Q = \ln A$ (poises) in Eq. (3).

Table 5. Activation Energies of E_a and E_η at the Two Characteristic Material States during the Cure of Hercules 3501-6 resin system

| Material State | E_a (kcal/mole) | E_η (kcal/mole) |
|-----------------|-------------------|----------------------|
| Gelation Point | 19.3 | 15.3 |
| Crossover Point | 22.0 | 26.2 |

Table 6. Rate Constants at Different Reaction Zones during the Isothermal Curing of Hercules 3501-6 Resin System

| T(°K) | G'(t) Curve | | G''(t) Curve | |
|-------|---------------------------|---------------------------|---------------------------|---------------------------|
| | $k_{po}(\text{min}^{-1})$ | $k_{pc}(\text{min}^{-1})$ | $k_{po}(\text{min}^{-1})$ | $k_{pc}(\text{min}^{-1})$ |
| 375 | - | - | - | - |
| 385 | 0.035 | - | 0.015 | - |
| 400 | 0.072 | 0.018 | 0.033 | 0.017 |
| 410 | 0.14 | 0.020 | 0.068 | 0.024 |
| 425 | 0.27 | 0.034 | 0.120 | 0.040 |
| 435 | 0.48 | 0.051 | 0.241 | 0.053 |

Table 7. Shift Factors $a_t(T)$ and $a_\eta(T)$ as Defined by Eqs. (6) and (7) for the Correspondence Effects of during Temperature and Time on the Hercules 3501-6 Resin System

| $T(^{\circ}\text{K})$ | $1/T (10^{-3} \text{ }^{\circ}\text{K}^{-1})$ | $a_t(T)$ | $a_\eta(T)$ |
|-----------------------|---|----------|-------------|
| 375 | 2.67 | 3.0 | 2.51 |
| 385 | 2.60 | 2.0 | 1.30 |
| 400 | 2.51 | 1.0 | 1.0 |
| 410 | 2.44 | 0.60 | 0.85 |
| 425 | 2.35 | 0.25 | 0.57 |
| 435 | 2.30 | 0.13 | 0.60 |

LIST OF FIGURES

| Figure | Captions |
|--------|---|
| 1 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 375 °K. |
| 2 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 385 °K. |
| 3 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 400 °K. |
| 4 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 410 °K. |
| 5 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 425 °K. |
| 6 | Storage modulus G' and Loss modulus G'' as functions of time for Hercules 3501-6 resin cured at 435 °K. |
| 7 | Semi-logarithmic plots of $G'(t)$ for Hercules 3501-6 resin cured under six isothermal curing temperatures. (the gelation and crossover points are marked by arrows). |
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| 9 | Double logarithmic plots of $G'(t)$ for Hercules 3501-6 resin cured under six isothermal curing temperatures. |
| 10 | Double logarithmic plots of $G''(t)$ for Hercules 3501-6 resin cured under six isothermal curing temperatures. |

- 11 Master curing curve of $G''(t)$ for Hercules 3501-6 resin cured under isothermal conditions.
- 12 Arrhenius plots of the shift factors $a_t(T)$ and $a_\eta(T)$.
- 13 Master curing curve of $G'(t)$ for Hercules 3501-6 resin system cured under isothermal conditions.

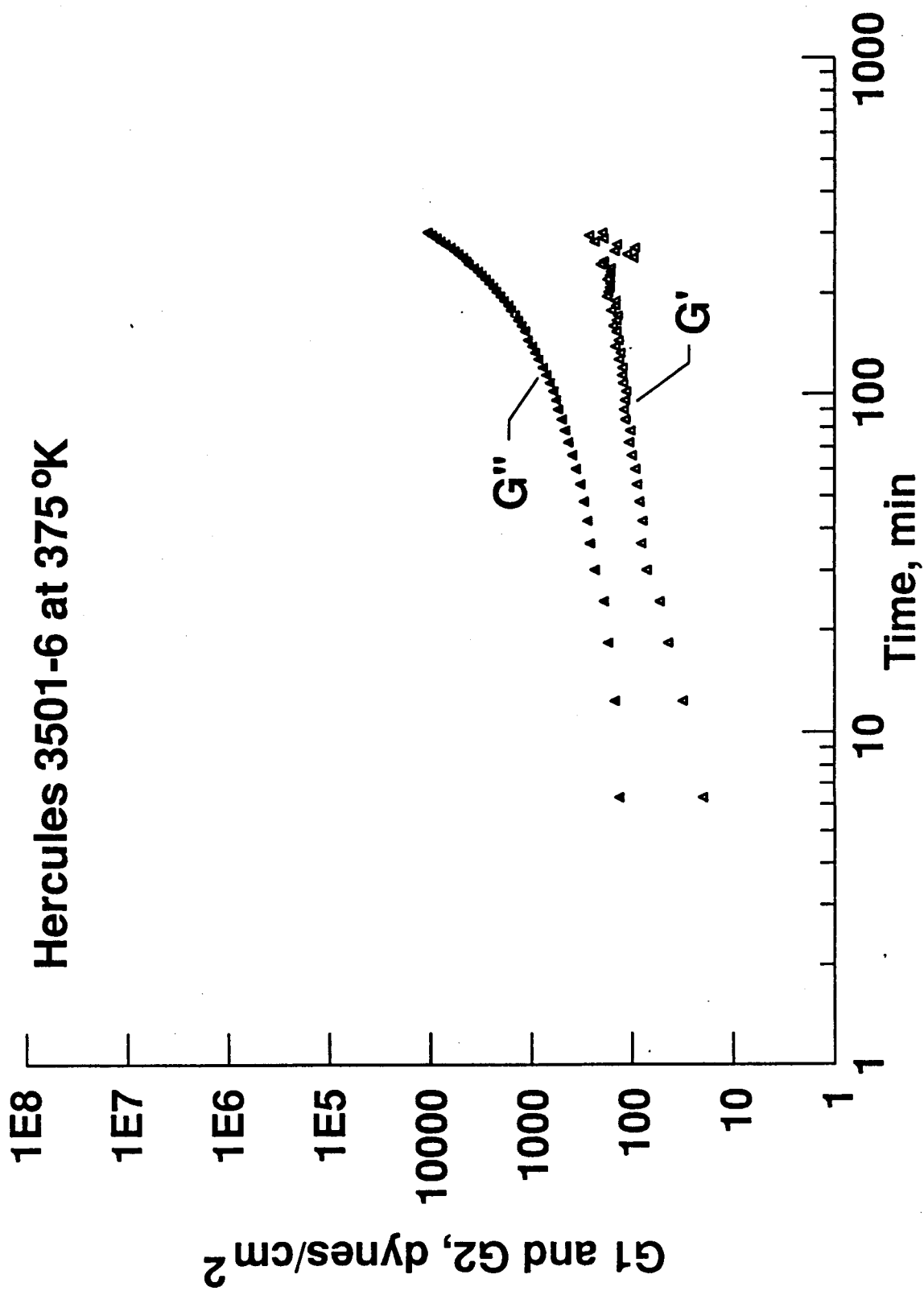


Figure 1

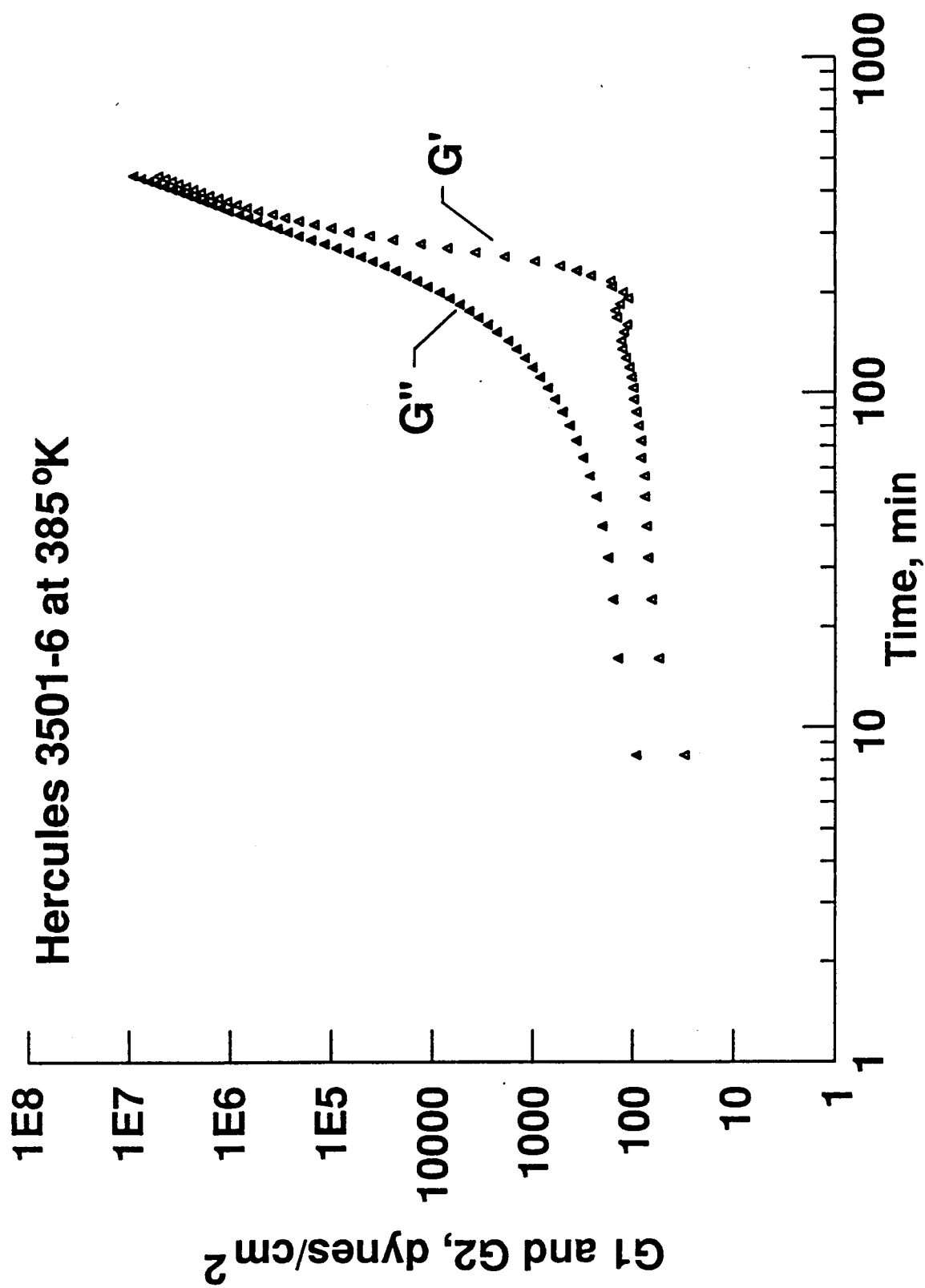


Figure 2

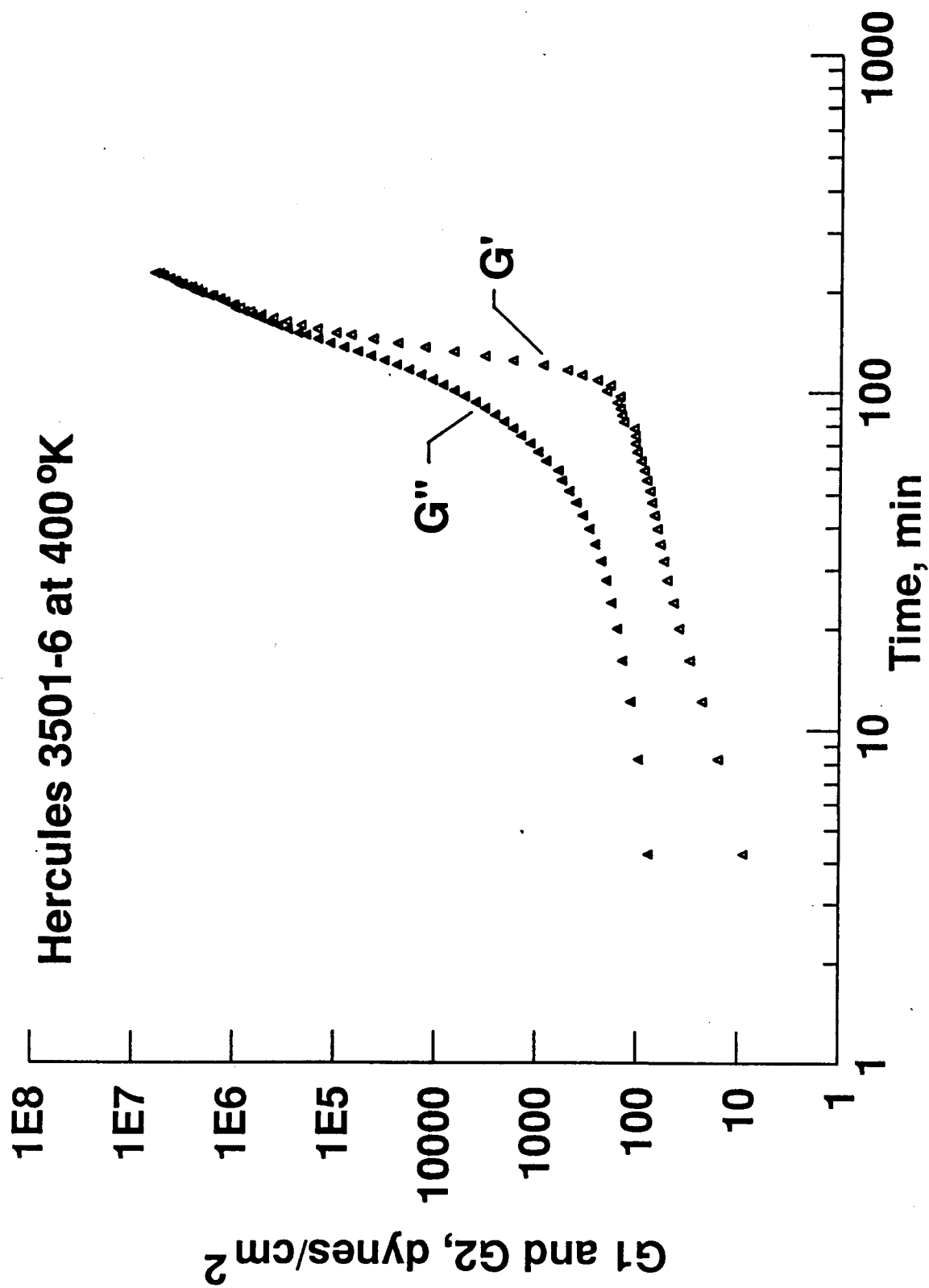


Figure 3

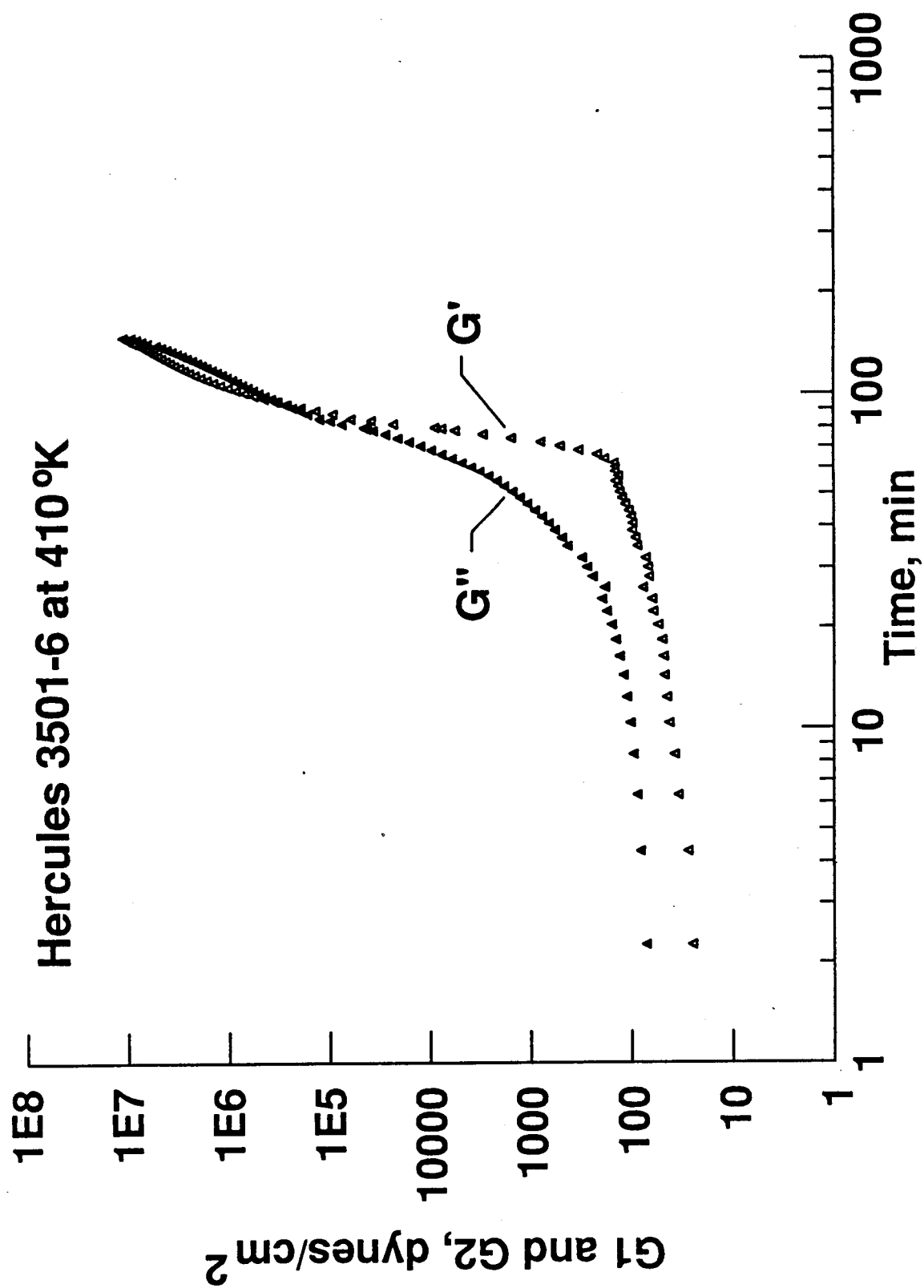
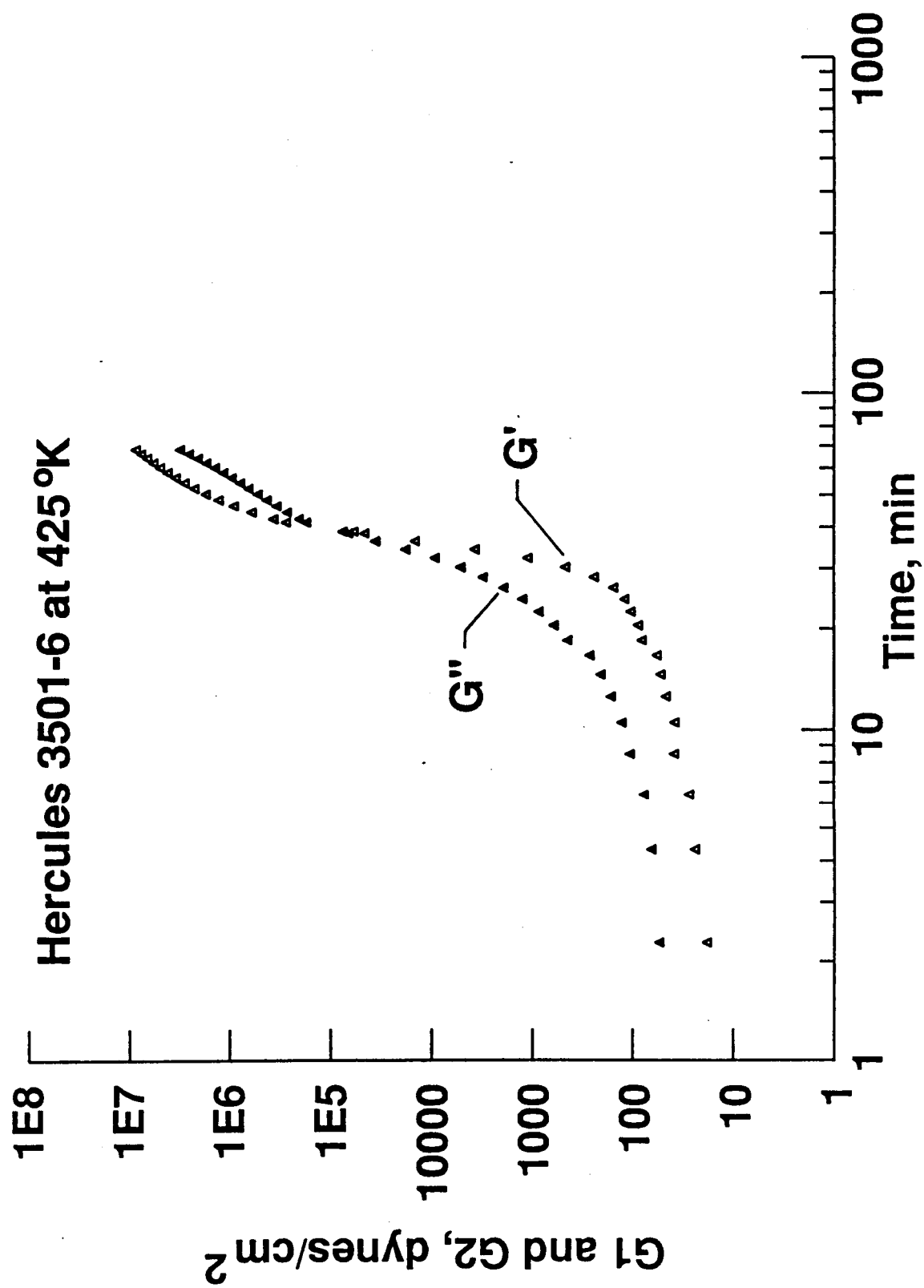


Figure 4



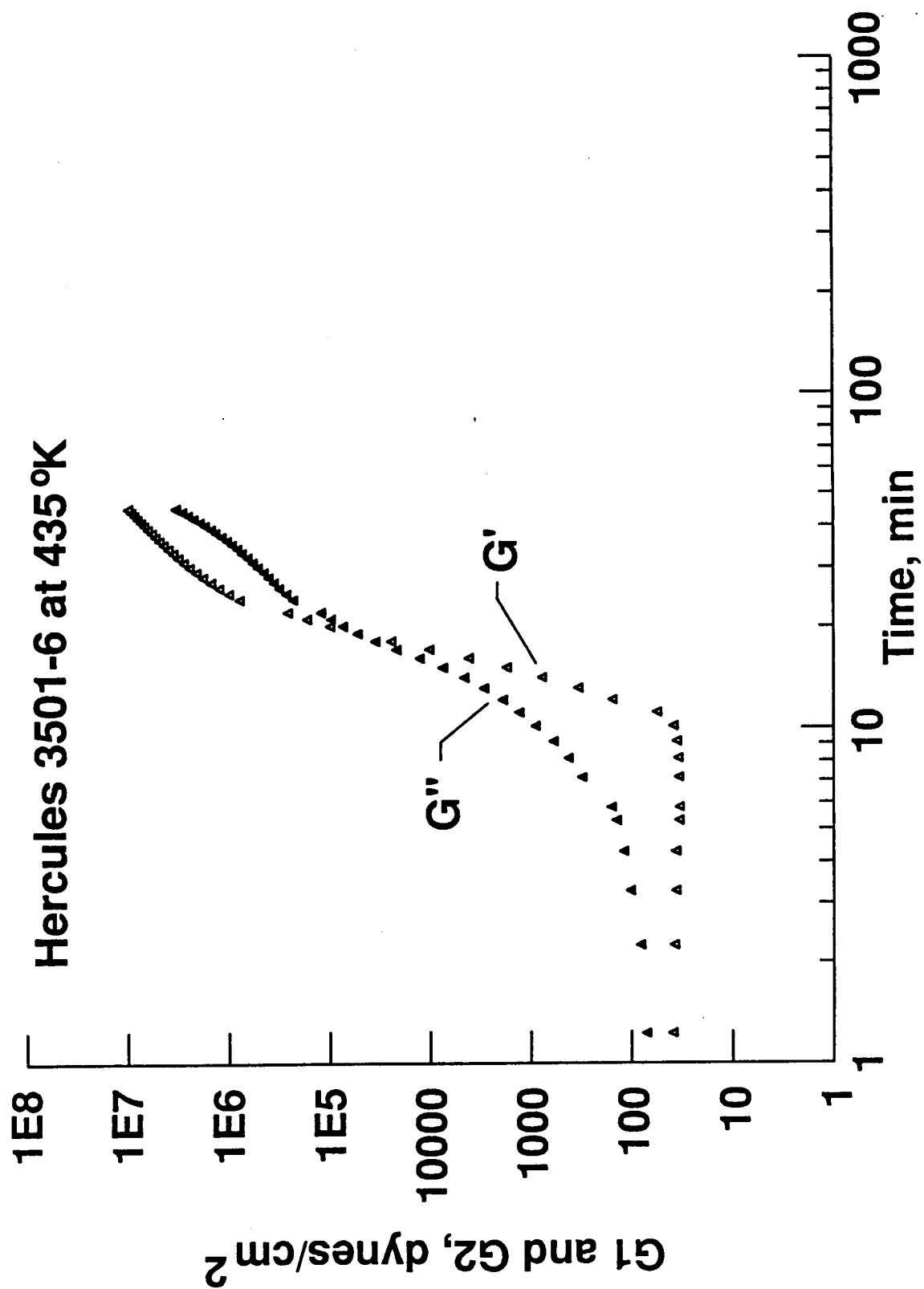


Figure 6

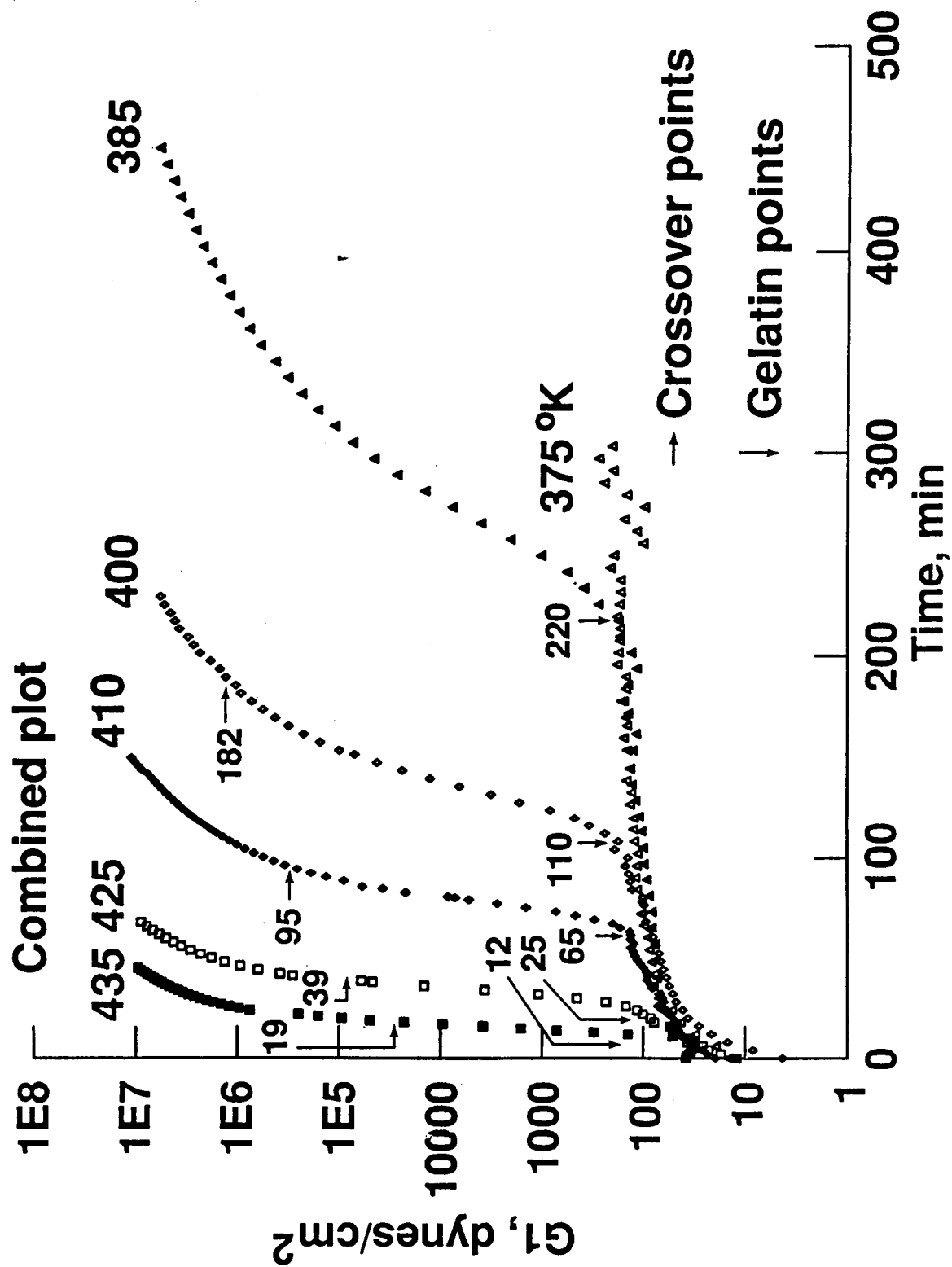


Figure 7

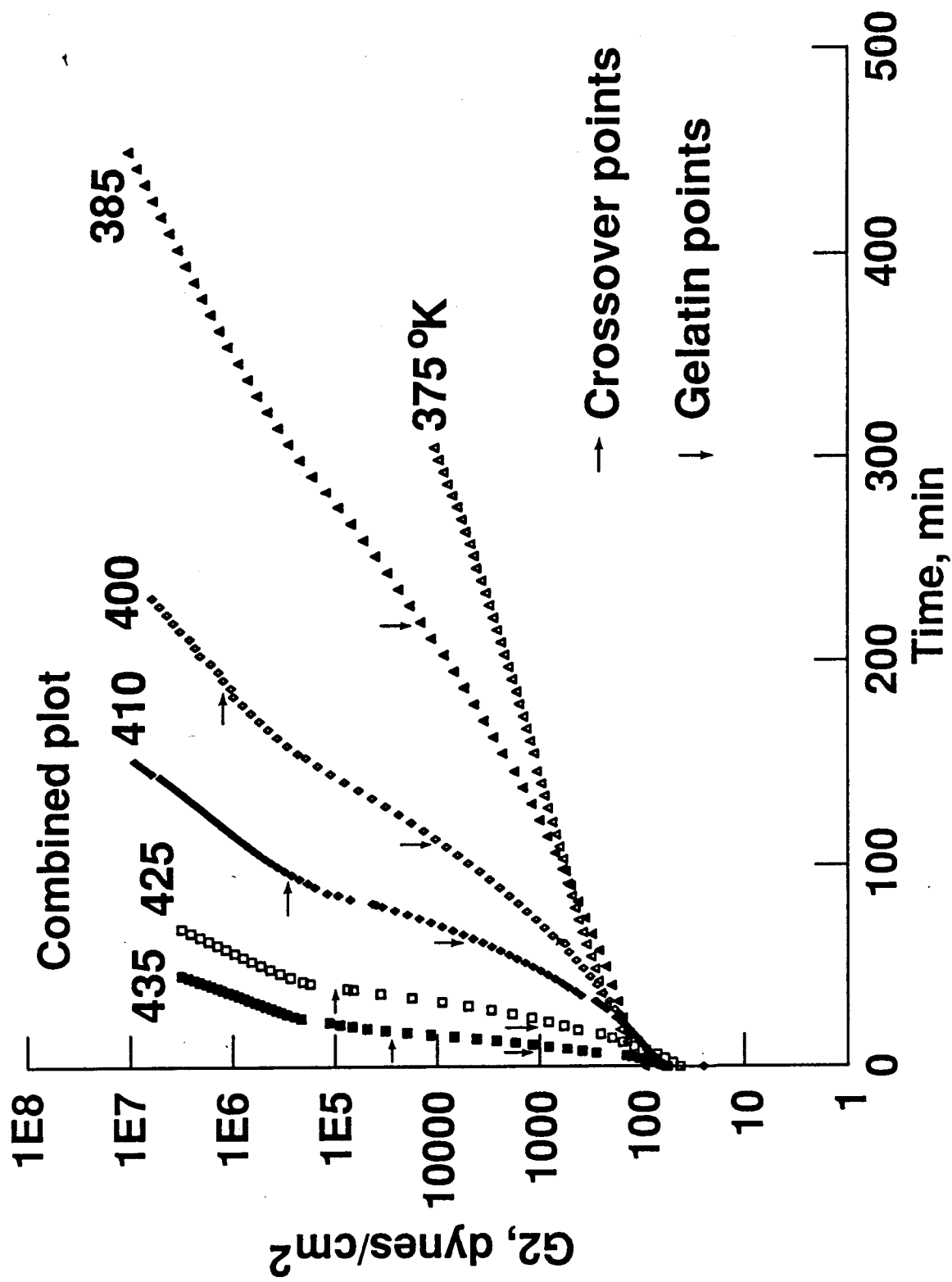
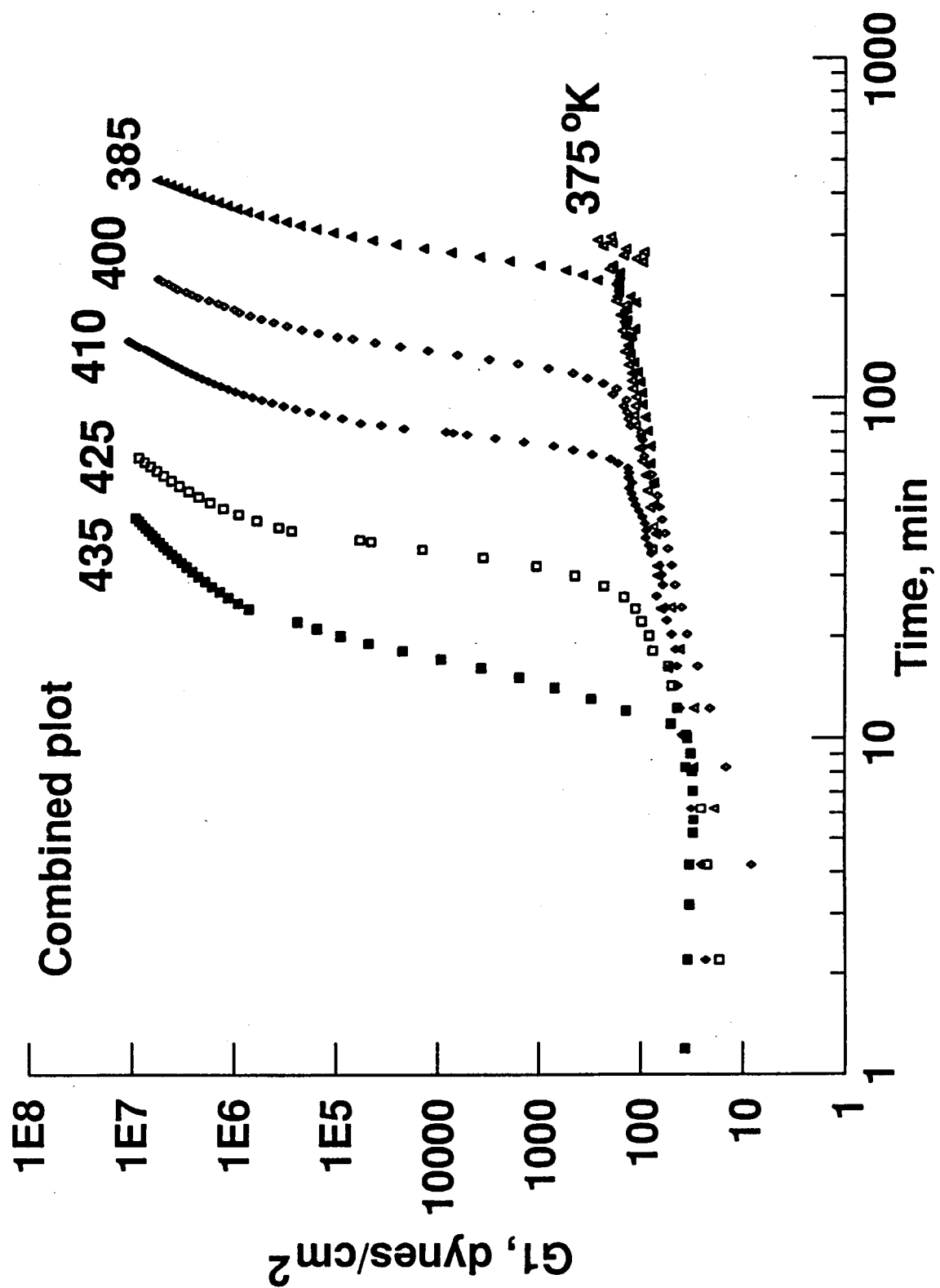


Figure 8



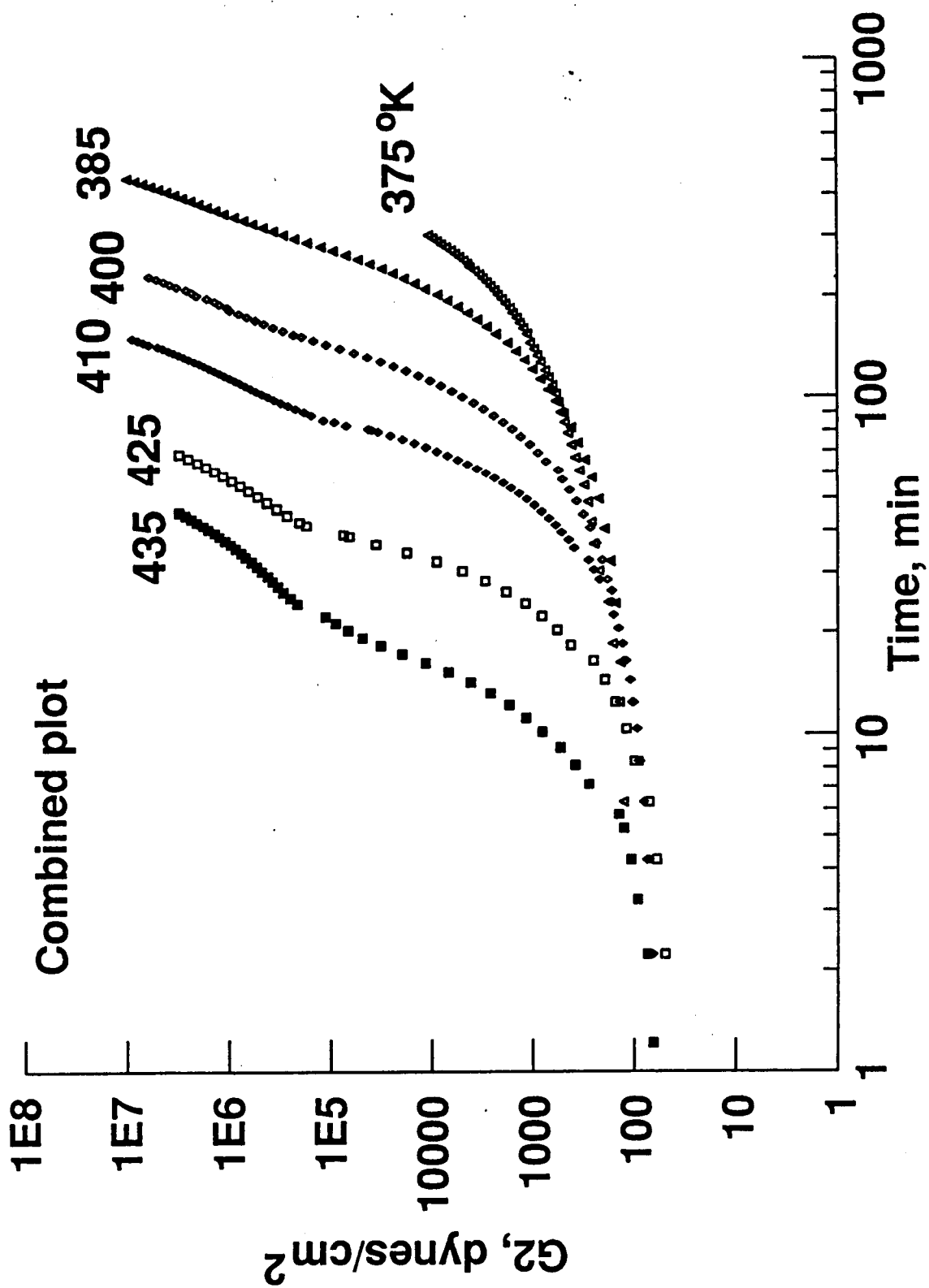


Figure 10

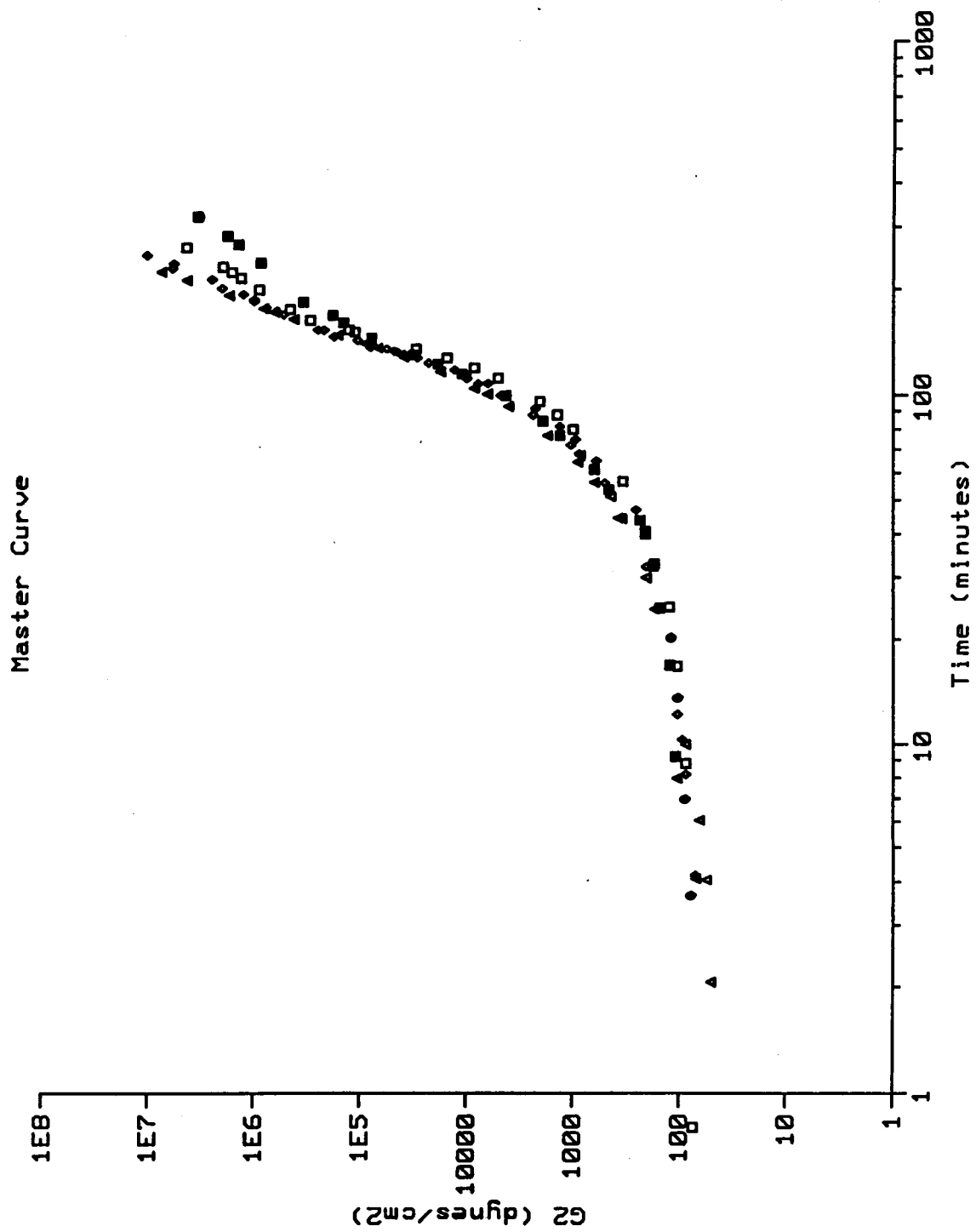


Figure 11

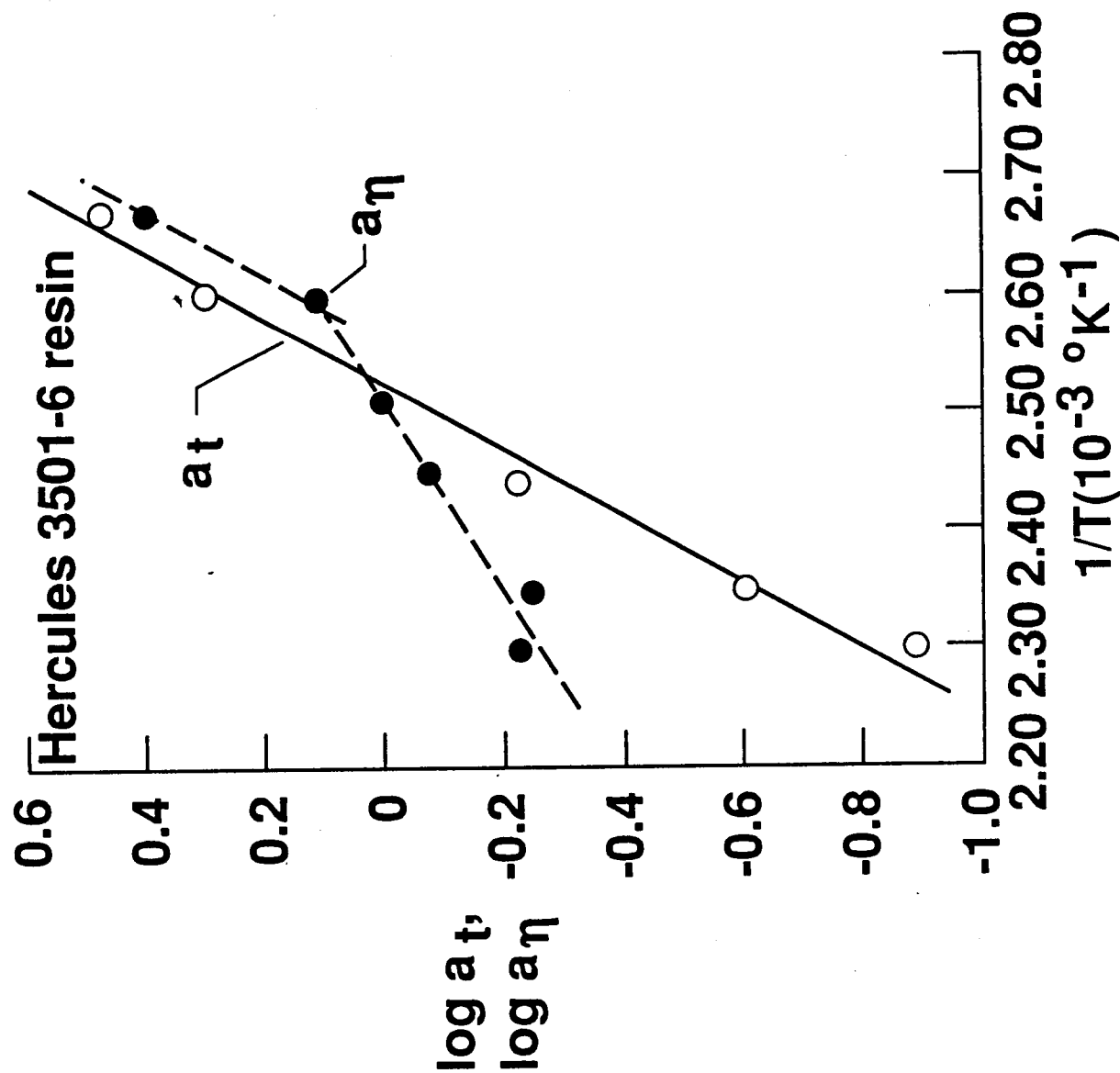


Figure 12

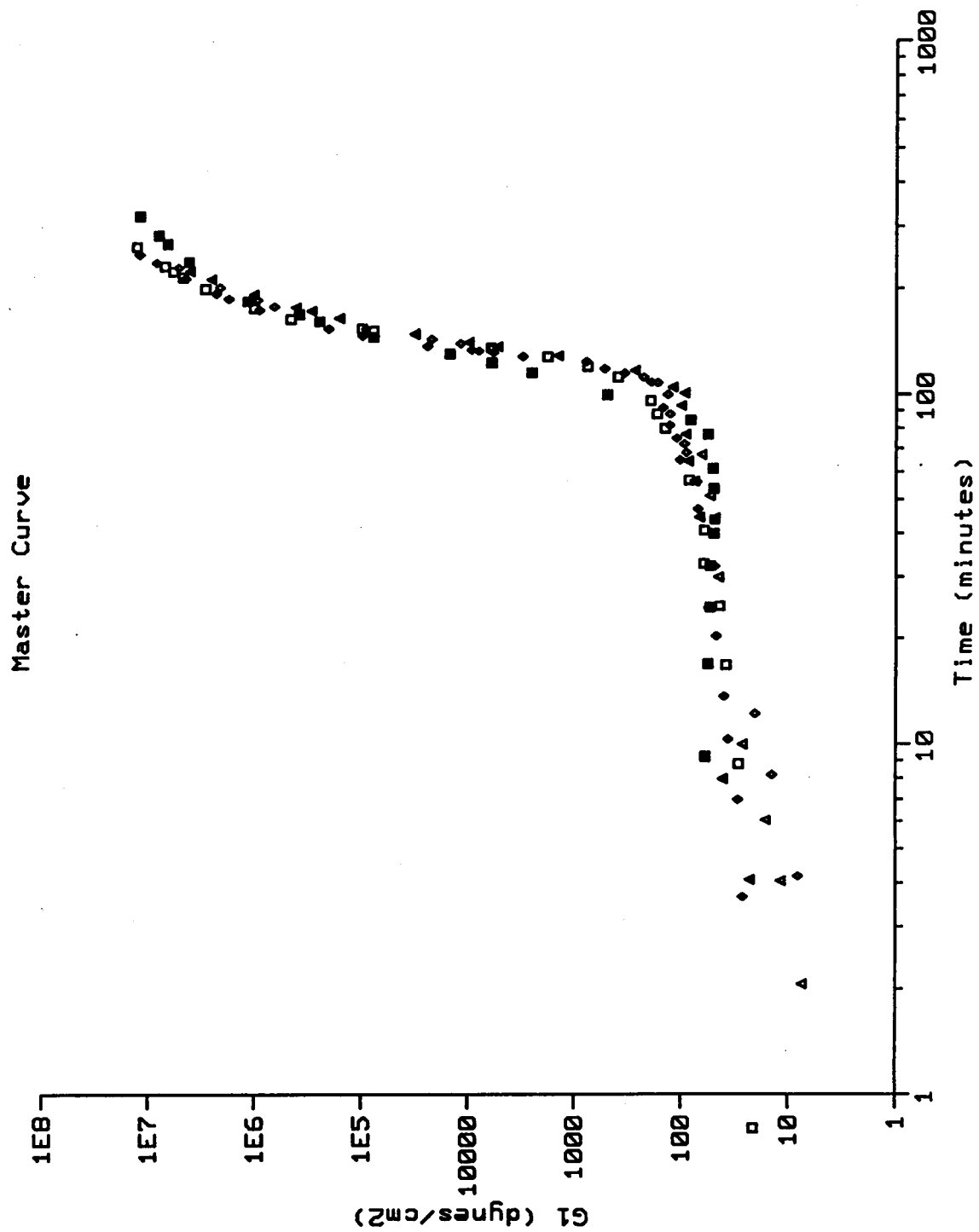


Figure 13

APPENDIX

Experimentally measured isothermal curing data reported in this study for the Hercules 3501-6 resin system are tabulated in the following pages:

```

c      Hercules 3501_6 resin cured at 375 K
51
c      Time(min)          G1          G2
c
0.2      1.132E1  9.094E1
6.2      1.805E1  1.22E2
12.2     2.838E1  1.346E2
18.2     3.963E1  1.562E2
24.2     4.81E1   1.72E2
30.0     6.511E1  2.121E2
36.0     7.346E1  2.371E2
42.0     7.163E1  2.515E2
48.0     7.705E1  2.725E2
54.0     8.119E1  2.967E2
60.0     8.441E1  3.289E2
66.0     9.17E1   3.588E2
72.0     9.754E1  3.916E2
78.0     9.514E1  4.229E2
84.0     1.064E2  4.552E2
90.0     1.101E2  4.972E2
96.0     1.076E2  5.184E2
102.0    1.05E2   5.549E2
108.0    1.128E2  5.997E2
114.0    1.148E2  6.506E2
120.0    1.142E2  7.074E2
127.0    1.237E2  7.81E2
133.0    1.194E2  8.46E2
139.0    1.342E2  9.084E2
145.0    1.246E2  9.963E2
154.0    1.319E2  1.069E3
160.0    1.422E2  1.156E3
166.0    1.309E2  1.255E3
172.0    1.271E2  1.346E3
178.0    1.48E2   1.477E3
184.0    1.346E2  1.574E3
190.0    1.338E2  1.736E3
196.0    1.634E2  1.893E3
202.0    1.577E2  2.068E3
208.0    1.527E2  2.233E3
214.0    1.517E2  2.431E3
220.0    1.622E2  2.657E3
226.0    1.537E2  2.901E3
232.0    1.498E2  3.147E3
238.0    1.497E2  3.469E3
244.0    1.882E2  3.908E3
250.0    1.75E2   4.109E3
256.0    8.961E1  4.45E3
262.0    1.034E2  4.946E3
268.0    1.364E2  5.389E3
274.0    8.635E1  5.925E3
280.0    1.299E2  6.64E3
286.0    2.162E2  7.416E3
292.0    1.769E2  8.091E3
298.0    2.447E2  9.048E3
304.0    1.814E2  9.957E3

```

c Hercules 3501_6 resin cured at 385 K

57

c Time(min) G1 G2

c

| | | |
|-------|---------|---------|
| 0.2 | 1.363E1 | 6.587E1 |
| 8.2 | 2.874E1 | 8.722E1 |
| 16.0 | 5.154E1 | 1.317E2 |
| 24.0 | 6.045E1 | 1.475E2 |
| 32.0 | 6.561E1 | 1.647E2 |
| 40.0 | 6.792E1 | 1.882E2 |
| 49.0 | 7.055E1 | 2.141E2 |
| 57.0 | 7.064E1 | 2.491E2 |
| 65.0 | 7.678E1 | 2.904E2 |
| 73.0 | 7.651E1 | 3.398E2 |
| 81.0 | 8.116E1 | 3.957E2 |
| 89.0 | 8.569E1 | 4.692E2 |
| 97.0 | 9.049E1 | 5.57E2 |
| 105.0 | 9.234E1 | 6.617E2 |
| 113.0 | 9.573E1 | 7.886E2 |
| 121.0 | 1.01E2 | 9.435E2 |
| 129.0 | 1.093E2 | 1.129E3 |
| 137.0 | 1.186E2 | 1.377E3 |
| 145.0 | 1.228E2 | 1.66E3 |
| 154.0 | 1.156E2 | 2.182E3 |
| 162.0 | 1.073E2 | 2.663E3 |
| 170.0 | 1.358E2 | 3.307E3 |
| 178.0 | 1.41E2 | 4.107E3 |
| 186.0 | 1.267E2 | 5.12E3 |
| 194.0 | 1.052E2 | 6.456E3 |
| 202.0 | 1.183E2 | 8.114E3 |
| 210.0 | 1.525E2 | 1.075E4 |
| 218.0 | 1.576E2 | 1.37E4 |
| 226.0 | 2.484E2 | 1.75E4 |
| 234.0 | 3.451E2 | 2.25E4 |
| 242.0 | 5.061E2 | 2.90E4 |
| 250.0 | 9.07E2 | 3.814E4 |
| 258.0 | 1.823E3 | 5.001E4 |
| 266.0 | 3.59E3 | 6.609E4 |
| 274.0 | 6.8E3 | 8.782E4 |
| 282.0 | 1.268E4 | 1.152E5 |
| 290.0 | 2.398E4 | 1.577E5 |
| 298.0 | 4.095E4 | 2.073E5 |
| 306.0 | 6.601E4 | 2.679E5 |
| 314.0 | 9.902E4 | 3.388E5 |
| 322.0 | 1.454E5 | 4.285E5 |
| 330.0 | 2.086E5 | 5.384E5 |
| 338.0 | 2.858E5 | 6.643E5 |
| 346.0 | 3.811E5 | 8.158E5 |
| 354.0 | 5.309E5 | 1.033E6 |
| 362.0 | 6.858E5 | 1.248E6 |
| 370.0 | 8.682E5 | 1.511E6 |
| 378.0 | 1.078E6 | 1.819E6 |
| 386.0 | 1.323E6 | 2.172E6 |
| 394.0 | 1.617E6 | 2.63E6 |
| 402.0 | 1.962E6 | 3.137E6 |
| 410.0 | 2.331E6 | 3.745E6 |
| 418.0 | 2.771E6 | 4.497E6 |
| 426.0 | 3.285E6 | 5.408E6 |
| 434.0 | 3.831E6 | 6.442E6 |
| 442.0 | 4.466E6 | 7.704E6 |

450.0 5.208E6 9.313E6

c Hercules 3501_6 resin cured at 400 K

59

c Time(min) G1 G2

c

| | | |
|-------|---------|---------|
| .2 | 4.142e0 | 2.474e1 |
| 4.2 | 8.062e0 | 7.000e1 |
| 8.2 | 1.421E1 | 8.674E1 |
| 12.2 | 2.043E1 | 1.037E2 |
| 16.2 | 2.7E1 | 1.256E2 |
| 20.2 | 3.438E1 | 1.41E2 |
| 24.2 | 3.896E1 | 1.609E2 |
| 28.2 | 4.523E1 | 1.813E2 |
| 32.2 | 4.883E1 | 2.042E2 |
| 36.2 | 5.315E1 | 2.338E2 |
| 40.2 | 5.667E1 | 2.674E2 |
| 44.2 | 6.055E1 | 3.116E2 |
| 48.2 | 6.431E1 | 3.632E2 |
| 52.2 | 6.71E1 | 4.259E2 |
| 56.2 | 7.209E1 | 5.019E2 |
| 60.2 | 7.607E1 | 5.467E2 |
| 64.2 | 8.223E1 | 7.238E2 |
| 68.2 | 9.014E1 | 8.691E2 |
| 72.2 | 9.43E1 | 1.046E3 |
| 76.2 | 9.36E1 | 1.289E3 |
| 80.2 | 9.662E1 | 1.563E3 |
| 84.0 | 1.225E2 | 1.922E3 |
| 88.0 | 1.283E2 | 2.379E3 |
| 92.0 | 1.324E2 | 3.0E3 |
| 96.0 | 1.428E2 | 3.742E3 |
| 100.0 | 1.345E2 | 4.835E3 |
| 104.0 | 1.818E2 | 6.115E3 |
| 108.0 | 1.675E2 | 7.867E3 |
| 112.0 | 2.259E2 | 1.007E4 |
| 116.0 | 3.224E2 | 1.313E4 |
| 120.0 | 4.477E2 | 1.742E4 |
| 124.0 | 7.806E2 | 2.312E4 |
| 128.0 | 1.568E3 | 3.107E4 |
| 132.0 | 3.017E3 | 4.223E4 |
| 136.0 | 6.165E3 | 5.719E4 |
| 140.0 | 1.2E4 | 7.831E4 |
| 144.0 | 2.26E4 | 1.069E5 |
| 148.0 | 4.007E4 | 1.422E5 |
| 152.0 | 6.683E4 | 1.858E5 |
| 154.0 | 9.37E4 | 2.228E5 |
| 158.0 | 1.44E5 | 2.83E5 |
| 162.0 | 2.085E5 | 3.538E5 |
| 166.0 | 2.924e5 | 4.363E5 |
| 170.0 | 3.961E5 | 5.303E5 |
| 174.0 | 5.236E5 | 6.421E5 |
| 178.0 | 6.728E5 | 7.716E5 |
| 182.0 | 8.574E5 | 9.489E5 |
| 186.0 | 9.626E5 | 1.004E6 |
| 190.0 | 1.205E6 | 1.195E6 |
| 194.0 | 1.382E6 | 1.332E6 |
| 198.0 | 1.704E6 | 1.582E6 |
| 202.0 | 2.167E6 | 2.008E6 |
| 206.0 | 2.5E6 | 2.233E6 |
| 210.0 | 2.833E6 | 2.529E6 |
| 214.0 | 3.45E6 | 3.146E6 |
| 218.0 | 3.807E6 | 3.657E6 |

| | | |
|-------|---------|---------|
| 222.0 | 4.21E6 | 4.19E6 |
| 226.0 | 4.825E6 | 4.954E6 |
| 230.0 | 5.274E6 | 5.852E6 |

c Hercules 3501_6 resin cured at 410 K

77

c Time(min) G1 G2

c

| | | |
|-------|---------|---------|
| 0.2 | 1.868E1 | 5.601E1 |
| 2.2 | 2.248E1 | 6.478E1 |
| 4.2 | 2.491E1 | 7.391E1 |
| 6.2 | 3.1E1 | 7.946E1 |
| 8.2 | 3.385E1 | 8.68E1 |
| 10.2 | 3.815E1 | 9.295E1 |
| 12.2 | 4.021E1 | 1.008E2 |
| 14.2 | 4.248E1 | 1.085E2 |
| 16.2 | 4.308E1 | 1.19E2 |
| 18.2 | 4.464E1 | 1.292E2 |
| 20.2 | 4.892E1 | 1.41E2 |
| 22.2 | 5.453E1 | 1.576E2 |
| 24.2 | 5.595E1 | 1.752E2 |
| 26.2 | 6.873E1 | 1.64E2 |
| 28.2 | 5.969E1 | 2.166E2 |
| 30.2 | 6.134E1 | 2.455E2 |
| 32.2 | 6.453E1 | 2.762E2 |
| 35.0 | 7.776E1 | 3.848E2 |
| 37.0 | 8.141E1 | 4.345E2 |
| 39.0 | 8.776E1 | 5.11E2 |
| 41.0 | 8.652E1 | 5.848E2 |
| 43.0 | 8.919E1 | 6.822E2 |
| 45.0 | 9.438E1 | 8.045E2 |
| 47.0 | 1.022E2 | 9.483E2 |
| 49.0 | 1.10E2 | 1.128E3 |
| 51.0 | 1.157E2 | 1.341E3 |
| 53.0 | 1.197E2 | 1.615E3 |
| 55.0 | 1.269E2 | 1.932E3 |
| 57.0 | 1.19E2 | 2.35E3 |
| 59.0 | 1.282E2 | 2.854E3 |
| 61.0 | 1.272E2 | 3.489E3 |
| 63.0 | 1.306E2 | 4.339E3 |
| 65.0 | 1.627E2 | 5.402E3 |
| 67.0 | 1.92E2 | 6.81E3 |
| 69.0 | 2.916E2 | 8.687E3 |
| 71.0 | 4.473E2 | 1.116E4 |
| 73.0 | 6.977E2 | 1.449E4 |
| 75.0 | 1.377E3 | 1.897E4 |
| 77.0 | 2.653E3 | 2.515E4 |
| 79.0 | 5.021E3 | 3.35E4 |
| 80.0 | 6.866E3 | 3.865E4 |
| 80.5 | 8.012E3 | 4.153E4 |
| 82.5 | 2.10E4 | 6.894E4 |
| 84.5 | 3.523E4 | 9.005E4 |
| 85.5 | 5.625E4 | 1.149E5 |
| 88.5 | 8.506E4 | 1.518E5 |
| 90.5 | 1.256E5 | 1.776E5 |
| 92.5 | 1.772E5 | 2.145E5 |
| 94.5 | 2.419E5 | 2.552E5 |
| 96.5 | 3.198E5 | 3.003E5 |
| 98.5 | 4.133E5 | 3.496E5 |
| 100.5 | 5.22E5 | 4.033E5 |
| 102.5 | 6.462E5 | 4.622E5 |
| 104.5 | 7.882E5 | 5.274E5 |
| 106.5 | 9.459E5 | 5.971E5 |
| 108.5 | 1.12E6 | 6.751E5 |

| | | |
|-------|---------|---------|
| 110.5 | 1.313E6 | 7.607E5 |
| 112.5 | 1.526E6 | 8.565E5 |
| 114.5 | 1.754E6 | 9.614E5 |
| 116.5 | 2.0E6 | 1.081E6 |
| 118.5 | 2.266E6 | 1.21E6 |
| 120.5 | 2.551E6 | 1.351E6 |
| 122.5 | 2.852E6 | 1.52E6 |
| 124.5 | 3.173E6 | 1.695E6 |
| 126.5 | 3.512E6 | 1.895E6 |
| 128.5 | 3.88E6 | 2.129E6 |
| 130.5 | 4.27E6 | 2.392E6 |
| 132.5 | 4.684E6 | 2.684E6 |
| 134.5 | 5.122E6 | 3.001E6 |
| 136.5 | 5.584E6 | 3.381E6 |
| 138.5 | 6.069E6 | 3.789E6 |
| 140.5 | 6.609E6 | 4.284E6 |
| 142.5 | 7.172E6 | 4.837E6 |
| 144.5 | 8.263E6 | 5.941E6 |
| 146.5 | 8.982E6 | 6.727E6 |
| 148.5 | 9.691E6 | 7.617E6 |
| 150.5 | 1.042E7 | 8.608E6 |

c Hercules 3501_6 resin cured at 425 K

36

c Time(min) G1 G2

c

| | | |
|------|---------|---------|
| 0.2 | 1.208E1 | 4.188E1 |
| 2.2 | 1.652E1 | 4.942E1 |
| 4.2 | 2.176E1 | 5.939E1 |
| 6.2 | 2.494E1 | 7.055E1 |
| 8.2 | 3.527E1 | 9.78E1 |
| 10.2 | 3.498E1 | 1.185E2 |
| 12.2 | 4.268E1 | 1.515E2 |
| 14.2 | 4.837E1 | 1.922E2 |
| 16.2 | 5.273E1 | 2.484E2 |
| 18.0 | 7.467E1 | 4.138E2 |
| 20.0 | 8.143E1 | 5.661E2 |
| 22.0 | 9.652E1 | 8.015E2 |
| 24.0 | 1.111E2 | 1.171E3 |
| 26.0 | 1.434E2 | 1.807E3 |
| 28.0 | 2.248E2 | 2.911E3 |
| 30.0 | 4.335E2 | 4.88E3 |
| 32.0 | 1.039E3 | 8.77E3 |
| 34.0 | 3.522E3 | 1.731E4 |
| 36.0 | 1.387E4 | 3.514E4 |
| 38.0 | 4.491E4 | 6.49E4 |
| 38.5 | 5.781e4 | 7.400e4 |
| 41.0 | 2.686e5 | 1.701e5 |
| 42.0 | 3.598E5 | 1.995E5 |
| 44.0 | 5.916E5 | 2.636E5 |
| 46.0 | 8.888E5 | 3.336E5 |
| 48.0 | 1.256E6 | 4.172E5 |
| 50.0 | 1.69E6 | 5.133E5 |
| 52.0 | 2.183E6 | 6.319E5 |
| 54.0 | 2.736E6 | 7.622E5 |
| 56.0 | 3.362E6 | 9.238E5 |
| 58.0 | 4.037E6 | 1.12E6 |
| 60.0 | 4.776E6 | 1.358E6 |
| 62.0 | 5.566E6 | 1.651E6 |
| 64.0 | 6.447E6 | 2.003E6 |
| 66.0 | 7.384E6 | 2.465E6 |
| 68.0 | 8.404E6 | 3.019E6 |

| | | | |
|------|--------------------------------------|---------|----|
| c | Hercules 3501_6 resin cured at 435 K | | |
| 45 | | | |
| c | Time(min) | G1 | G2 |
| c | | | |
| 0.2 | 3.639E1 | 5.563E1 | |
| 1.2 | 3.579E1 | 6.509E1 | |
| 2.2 | 3.382E1 | 7.342E1 | |
| 3.2 | 3.239E1 | 9.136E1 | |
| 4.2 | 3.229E1 | 1.059E2 | |
| 5.2 | 2.988E1 | 1.252E2 | |
| 5.7 | 2.949e1 | 1.394e2 | |
| 7.0 | 3.00e1 | 2.75e2 | |
| 8.0 | 3.051E1 | 3.752E2 | |
| 9.0 | 3.14E1 | 5.255E2 | |
| 10.0 | 3.393E1 | 7.966E2 | |
| 11.0 | 4.919E1 | 1.155E3 | |
| 12.0 | 1.363E2 | 1.693E3 | |
| 13.0 | 2.98E2 | 2.588E3 | |
| 14.0 | 6.831E2 | 4.057E3 | |
| 15.0 | 1.538E3 | 6.665E3 | |
| 16.0 | 3.659E3 | 1.131E4 | |
| 17.0 | 9.11E3 | 1.937E4 | |
| 18.0 | 2.185E4 | 3.157E4 | |
| 19.0 | 4.734E4 | 4.766E4 | |
| 20.0 | 8.926E4 | 6.644E4 | |
| 21.0 | 1.514E5 | 8.729E4 | |
| 22.0 | 2.356E5 | 1.1E5 | |
| 24.0 | 7.128E5 | 2.086E5 | |
| 25.0 | 9.039E5 | 2.441E5 | |
| 26.0 | 1.131E6 | 2.869E5 | |
| 27.0 | 1.366E6 | 3.228E5 | |
| 28.0 | 1.631E6 | 3.657E5 | |
| 29.0 | 1.904E6 | 4.076E5 | |
| 30.0 | 2.218E6 | 4.662E5 | |
| 31.0 | 2.529E6 | 5.239E5 | |
| 32.0 | 2.868E6 | 5.917E5 | |
| 33.0 | 3.223E6 | 6.766E5 | |
| 34.0 | 3.606E6 | 7.465E5 | |
| 35.0 | 4.0E6 | 8.424E5 | |
| 36.0 | 4.406E6 | 9.465E5 | |
| 37.0 | 4.826E6 | 1.074E6 | |
| 38.0 | 5.265E6 | 1.228E6 | |
| 39.0 | 5.735E6 | 1.367E6 | |
| 40.0 | 6.233E6 | 1.57E6 | |
| 41.0 | 6.727E6 | 1.754E6 | |
| 42.0 | 7.277E6 | 2.035E6 | |
| 43.0 | 7.824E6 | 2.295E6 | |
| 44.0 | 8.403E6 | 2.633E6 | |
| 45.0 | 9.036E6 | 3.027E6 | |

Report Documentation Page

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|--|--|--|---|--|--|
| 1. Report No. NASA CR-181807 | | 2. Government Accession No. | | 3. Recipient's Catalog No. | |
| 4. Title and Subtitle Chemoviscosity Modeling for Thermosetting Resin Systems - IV | | | | 5. Report Date March 1989 | |
| | | | | 6. Performing Organization Code | |
| 7. Author(s) T. H. Hou and Joan Y. Z. Huang | | | | 8. Performing Organization Report No. | |
| | | | | 10. Work Unit No. 505-63-01-01 | |
| 9. Performing Organization Name and Address Planning Research Corporation PRC Systems Services 303 Butler Farm Road Hampton, VA 23666 | | | | 11. Contract or Grant No. NAS1-18000 | |
| | | | | 13. Type of Report and Period Covered Contractor Report | |
| 12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Langley Research Center Hampton, VA 23665-5225 | | | | 14. Sponsoring Agency Code | |
| | | | | | |
| 15. Supplementary Notes T. H. Hou, Planning Research Corporation, 303 Butler Farm Road, Hampton, VA 23666; Joan Y. Z. Huang, Dept. of Mechanical Engineering and Mechanics, Old Dominion University, Norfolk, VA 23508. Langley Technical Monitor: R. M. Baucom | | | | | |
| 16. Abstract An experimental study on the changes of chemorheological properties has been conducted and analyzed on commercial Hercules 3501-6 resin system cured under several isothermal conditions between 375 and 435°K. For the cure temperatures $\geq 385^\circ\text{K}$, the storage modulus curing curves, $G'(t)$, exhibited abrupt changes in slope which occurred at various times depending on the curing temperatures and were attributed to the onset of gelation reactions. The crossover points between $G'(t)$ and $G''(t)$ curves were observed for curing temperatures $\geq 400^\circ\text{K}$. The gelation and the crossover points obtained from the chemorheological measurements, therefore, defined two characteristic resin states during cure. Approximately the same value for the degree of cure was reached by the advancement of the reaction at each of these states. The temperature dependency of the viscosities for the characteristic resin states and the rate constants of increase in moduli at different stages of curing were analyzed. Various $G'(t)$ and $G''(t)$ isothermal curing curves were also shown to be capable of being superimposed on one another by the principle of time-temperature superposition. The resultant shift factors $a_t(t)$ and $a_\eta(T)$ were shown to follow the Arrhenius type relationship. Values of the activation energy suggested that the reaction kinetics, instead of the diffusion mechanism, was the limiting step in the overall resin advancement for the cure at temperatures $\geq 385^\circ\text{K}$. | | | | | |
| 17. Key Words (Suggested by Author(s)) Chemorheology Chemoviscosity Modeling Thermosetting Resin | | | 18. Distribution Statement Unclassified - Unlimited Subject Category 24 | | |
| 19. Security Classif. (of this report) Unclassified | | 20. Security Classif. (of this page) Unclassified | | 21. No. of pages 50 | |
| | | | | 22. Price A03 | |